Ortho-Chain-Bridged Polyacetylene via the Ring-Opening Metathesis Polymerization

Thesis by

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To those who encouraged me

ABSTRACT

Chain-bridged poly(acetylene) polymers have previously been synthesized with meta- and para- linkages to the substituents. In this paper, two ortho-chain-bridged poly(cyclooctatetraene) polymers demonstrate the effects of an enforced cis linkage approximately every fourth carbon-carbon double bond in a poly(acetylene)-like polymer.

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I. Introduction

Conducting polymers continue to be a major area of research due to their possibilities in photovoltaic devices.[2] Poly(acetylene) has an extended conjugated π-system, but is insoluble and difficult to process.[3] Some substituted poly(acetylenes) from polymeriztion of substituted alkymes are soluble, but have lower conductivities that are in the range of non-crystalline poly(acetylenes).[4] Most of these polymers, in the predominantly trans configuration, are know to be insoluble, and therefore difficult to process. When the cis configuration predominantes, most substituted poly(acetylenes) and poly(cyclooctatetraenes) [poly(COT)] are soluble, but as a result appear to have shorter conjugation lengths based on the red shift seen in the measurements of their optical-absorption maximum (λ_{max}, nm) versus the trans configuration.[5]

Theoretically, if a poly(acetylene) chain is planar, it should have an infinite conjugation length due to extended p-orbital overlap, independent of its configuration (cis or trans). If the p electron delocalization were complete and the carbon-carbon bond lengths were equivalent, the separation between the π and π^* bands would be zero and, therefore the band gap would be zero.[6] Yet, the system is instable towards a Peierel's transition, because of the short carbon-carbon double bonds and long carbon-carbon single bond alternation, and results in a non-zero band gap.

In the case of mono-substituted poly(acetylenes), the carbon to which the substituent is attached is thought to twist the chain out of planarity.[7] Traettenberg[8] reports electron diffraction data which imply that the all-trans isomer of 1,3,5-hexatriene is planar, but the all-cis isomer is non-planar, with a 10 degree twist about the central double bond. Similar effects may be observed with incorporation of cis double bonds into the polymer main chain. This same idea is supported by UV studies done by Gavin, Jr., Risemberg and Rice[9] whose results using molecular orbital calculations suggest a lower energy ground state to excited state transition of trans hexatriene relative to the cis isomer, which may be attributed to an out of plane torsion of the molecule. Longer biopolyenes also show a shorter wavelength in their UV-Vis spectra

when a cis bond occurs in the molecule.[10] These results imply that not only incorporation of substituents cause an out of plane twist, but also incorporation of a cis bond induces a twist in a poly(acetylene)-like backbone. With the enforced cis bond, the Peierls distortion is more difficult to overcome due to a greater barrier to rotation around the fused bond where solitons are created via doping of the polymer. In the case of non-chain-bridged poly(acetylene), the bond lengths become equivalent around the region of the soliton due to easier rotation of each bond leading to isomerization from the cis to the trans form. These are different types of polyenes, so they should not be directly compared, but the general trend is that a cis bond in a polyene chain twists the chain out of planarity.

In an effort to better understand these chain-bridged poly(acetylene) systems, one cis bond on the average of every fourth carbon-carbon double bond is incorporated in the poly(acetylene) backbone by ortho-fusion to a benzene or 1,4-dihydrobenzene ring in this new system (Figure 1).

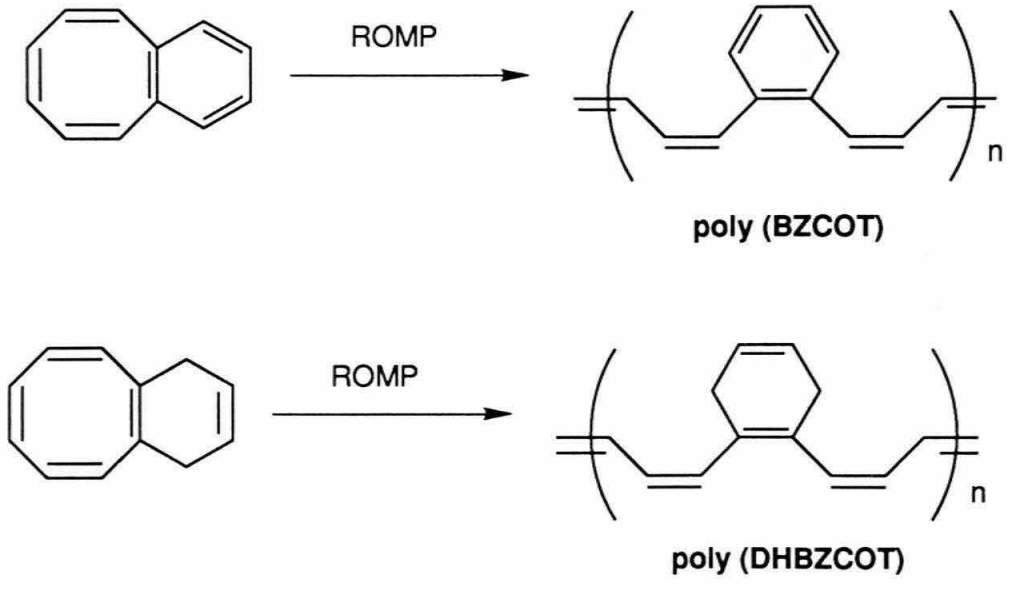


Figure 1: ortho-chain bridged polymers

This was achieved by synthesizing the monomers,1,4 - dihydrobenzene-cyclooctatetraene and benzocyclooctatetraene, and

subsequently performing ring-opening metathesis polymerization (ROMP) of the monomer to obtain the desired polymer. The purpose of this study is to determine if one enforced cis double bond every repeat unit of the poly(COT) is sufficient to keep the polymer soluble after isomerization to its predominantly trans form. The enforced cis bond may disrupt the conjugation length and/or inhibit the propagation of charge carriers in the doped polymers and will then serve as a probe of the effects of chain geometry on the conductivity of poly(acetylenes).

II. Experimental

General: Air and/or water sensitive compounds were handled with standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres Dry Box. NMR spectra were recorded with a JEOL GX-400 (399.65 MHz ^{1}H, 100.40 MHz ^{13}C) spectrometer. Gel permeation chromatography was performed with a home-built system consisting of three Styragel columns, an Altex Model 110A pump and a Knauer differential refractometer using methylene chloride as an eluent with a flow rate of 1.0 mL/minute at room temperature. Conductivity measurements used a four-point probe apparatus in a nitrogen-filled dry box. UV-Vis measurements were measured on a Hewlett Packard 8254 Diode Array instrument in benzene and THF. Electrochemical experiments were performed in a nitrogen-filled dry box using a PAR-179 potentiostat and PAR-175 programmer. Voltammetry was performed using a 3-electrode configuration in a 1-compartment cell. The non-aqueous reference electrode was Ag/Ag^{+}, and potentials were referenced to SCE by calibration with the Fe/Fe^{+} couple (420mV versus SCE. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-7, and thermogravimetric analysis on a Perkin -Elmer TGA-2. The powder X-ray diffraction instrument had a Guiner camera with a camera constant of 0.35827°/min, using CuK_a radiation.

Benzene, diethyl ether, pentane, tetrahydrofuran were either distilled or vacuum transferred from sodium benzophenone ketyl . Methylene chloride was vacuum transferred from P_2O_5. All solvents were degassed using the freeze-pump-thaw method before use.

Final products were stored under an inert atmosphere below room temperature to prevent decomposition. COT was a generous gift from BASF and stored in the freezer to prevent decomposition.

Monomer synthesis: 1,4-dihydrobenzenecyclooctatetraene (DHBZCOT) was prepared from bromocyclooctatetraene (BrCOT)[11,13] by conversion to the cyclooctatriene-yne and performing a Diels-Alder reaction with 1,3-butadiene as described in the literature.[12] DHBZCOT is a yellow oil at room temperature. DHBZCOT could later be oxidized to benzocyclooctatetraene (BZCOT) with 1,2-dichloro-4,5-dicyano-benzoquinone (DDQ). The resulting white solid had a melting point at 47.8-48.1°C in agreement with the literature[13] and was stored in the same manner as describe above. The ^{1}H NMR spectroscopic data for the two compounds was in accord with the literature data.[14]

Polymer Synthesis:

a) poly-DHBZCOT: Under a nitrogen atmosphere, the catalyst, W(CHPh)(NAr)[OCMe(CF_3)$_2$]$_2$[15] was added neat to the monomer in a 100:1 molar monomer to catalyst ratio. The reaction was thoroughly mixed and allowed to react, on average, for two hours. The reaction mixture would become orange-brown in color and viscous within 30 seconds. Although the mixture darkened in color, it never solidified. The polymer was then end-capped with 10 molar equivalents of benzaldehyde and dissolved in benzene to wash out any catalyst residue. The polymer was precipitated with pentane and methanol, the excess solvent was removed via cannula and the remaining orange film was dried in vacuo for several hours to remove any residual monomer, and backbiting products such as benzene and 1,4-dihydro-napthalene. ^{1}H NMR and GPC shows signs of residual monomer, even after several washings and precipitations with pentane.
GPC (CH_2Cl_2): M_w = 26-173K, M_n = 11-53K, PDI = 2.25-3.23

b) poly-BZCOT: A similar procedure was followed here; except, the monomer and catalyst were dissolved in a minimal amount of

benzene (100mL per 100mg monomer) prior to polymerization. Work up of the reaction was the same and residual monomer is also seen in the ^1H NMR and GPC.
GPC (CH_2Cl_2): M_w = 73-161K, M_n = 32-110K, PDI = 1.51-4.97

Isomerization: Isomerization from a predominantly cis to a predominantly trans composition of each polymer was performed by exposing the polymer, as a benzene solution, at 0°C to a Pyrex filtered, 350 watt, medium pressure Hanovia lamp. Irradiation was continued until no further change was observed in the visible absorption spectrum. Prolonged exposure past this point resulted in the formation of a solid, which is thought to be aggregation of the predominately trans polymer chains because the absorption UV spectra of the polymer solution was similar to the reference cell. Cis to trans isomerization also occurs over the course of a few days exposed to room light.

Films: Poly(BZCOT) films are yellow (cis) to yellow-brown (trans) in color, and poly (DHBZCOT) films are orange (cis) to red-orange (trans). Both polymers are flexible and can be stretched after initial formation of the film. Films are made by dissolving freshly prepared predominately cis polymer into a small amount of THF or benzene and casting the solution on to a glass slide with a pipet. After the solvent has evaporated, the films can be removed and are free standing. Film thickness can be increased by layering of polymer solutions upon one another in the above manner.

Electrochemistry[16] : Voltammetry was performed on glassy carbon electrodes modified with a thin film of polymer cast from a methylene cloride solution. A 3-electrode configuration was used in a 1-component voltammetry cell containing 0.1M acetonitrile in tetra-ethyl ammonium butyl tetra-fluoride ($TEABF_4$). The reference electrode was Ag/Ag^+. All electrochemical experiments were performed in a nitrogen-filled dry box.

Doping and Conductivity Measurements: The films were on the

average of 10-13 micrometers thick. The films were doped by vapor phase iodine until saturation (24 hours), and residual I_2 was removed under vacuum < 1mm torr (24 hours). Conductivity measurement were done with a four point probe apparatus in air and under nitrogen atmosphere in the dry box.

III. **Results and Discussion**

The properties observed in these polymers are consistent with other substituted poly(acetylenes). UV studies show a moderate conjugation length of the initial polymer made via ROMP based on previous studies of poly(COT)s. The UV absorbtion of poly(COT)s ranges from 302-538 nm for polymers in a predominately cis form, and 432-634 nm for the same polymers in a predominately trans form. The λ_{max} of predominately cis poly(BZCOT) and poly (DHBZCOT) occurs at 372 nm and 368 nm respectively . As the polymer is photoisomerized, the UV spectra are red shifted on the average of 30 nm for poly-BZCOT (400 nm) and 75 nm for poly-DHBZCOT (444 nm). This suggests a change in the polymer's configuration from predominately cis to predominately trans.[17] In the case of poly(DHBZCOT), an isosbestic point at 398 nm is observed which is characteristic of the polymer chains isomerizing simultaneously from cis to trans, similar to poly(TMSCOT). It can be seen in the spectrum that as the shorter wavelength decreases in absorbance, the trans grows in equal amounts. When both polymers are isomerized in benzene, the polymer chains aggregate, or possibly cross-link, and precipitate out of solution as yellow flakes. The same phenomena occurs in THF for poly(BZCOT). The UV spectrum shows no isosbestic point, just a 30 nm shift. With each spectrum taken after one minute of exposure to the mercury lamp, the level of absorbance decreases and a yellow precipitate is observed.

The high energy λ_{max} in the electronic spectra, suggests a disruption of the pi-orbital overlap in both polymers. The benzene substituent in poly(BZCOT) is known to be planar, and 1,4-dihydrobenzene, via NMR studies[18] , is thought to be almost planar. A twist in the backbone could be due to interactions of the H-atoms in the ortho position of the rings with those on the backbone.

(Figure 2).

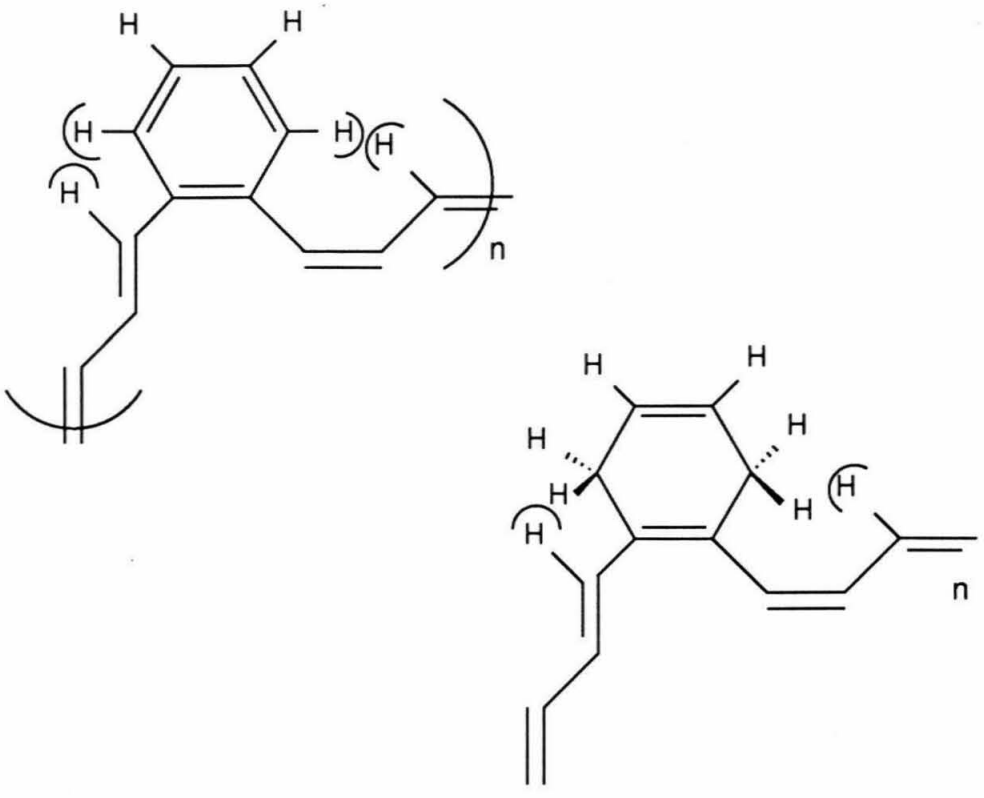


Figure 2: Backbone hydrogen and ring hydrogen interactions

Similar interactions cause a 23° twist between two benzene rings in poly-(para-phenylene).[19] On this basis, it seems reasonable that the ortho fused 1,4-dihydrobenzene ring approaches a planar configuration in order to minimize the hydrogen interactions. Twisting of the backbone out of planarity is also caused by the enforced cis bond.[20] However, it is unlikely that the two effects can be unambiguously separated.

Differential Scanning Calorimetry does not show an exotherm, which may be assigned to the isomerization of the polymer from a predominately cis to a predominately trans configuration. The isomerization temperature for most substituted poly(COT)s isomerize at 100-165°C. Attempted thermal isomerization in solution lead only to decompisition of the polymer. Thermal gravimetric analysis shows that the polymers begin to lose weight at 110°C, demonstrating very little thermal stability. The

mechanism for isomerization is still thought to be similar to biopolyenes which "unkink" a series of cis double bonds simultaneously as opposed to sequentially, until the chain has been "straightened out" to a predominately trans configuration.[21] However, shorter conjugation lenghts isomerize less easily in the solid state than longer conjugation lengths,[22] and the UV studies done on both poly(BZCOT) and poly(DHBZCOT) demonstrate shorter conjugation lengths than most poly (COT)s.

Predominately cis polymer is soluble in a variety of organic solvents, and the predominately trans polymer appears to be insoluble. Obviously, it takes more than one cis bond every fourth carbon-carbon double bond to create a soluble polymer. After polymerization, residual monomer and backbiting product, napththalene or 1,4-dihydro-napthalene, are present according to the ^{1}H NMR spectra. To prevent the formation a backbiting product, polymerizations were carried out in the minimal amount of solvent possible. It was not possible to calculate the percentage of backbiting due to the overlapping of the polymer, monomer, and napthalene ^{1}H NMR peaks . Films were made from predominately cis polymer and found to be amorphous by X-ray diffraction. This also applies to the powder collected after precipitation upon photoisomerization.

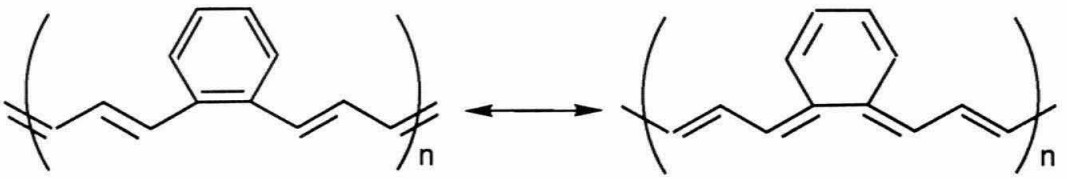
Upon doping fresh, predominately cis films with iodine, the polymers display moderate conductivities, when measured in air: 2.5×10^{-3} S/cm for poly-DHBZCOT and 3×10^{-6} S/cm for poly-BZCOT. When measured in a dry box, no discernable conductivities are observed. This is similar to poly(1,6-heptadiyne) where conductivity increases by a factor of 10^3 upon exposureto oxygen and rapidly loses all conductive properties within a few hours.[23] It is known that isomerization to the trans configuration occurs upon doping.[24] Polymer films are brittle when first doped and lose all conductivity within twenty-four hours after being exposed to air. The observed macroscopic conductivities suggest that the moderate conjugation lengths of the polyene backbone are sufficient to allow soliton formation; although, interchain interactions must be operative as well.[25] Torsions of the chains could also decrease

interchain interaction necessary for manifestation of bulk conductivity creating a high degree of internal resistance to charge propagation. However, there are no other chain-bridged poly(acetylene) systems of this nature with which to compare the general conductivities of poly(BZCOT) and poly (DHBZCOT). The most common chain-bridged systems[26] are either meta- or para-substituted rings attached in series like poly(1,6-heptadiene) and poly-(para-phenylene).

One theory predicts that the solitons[27] formed upon doping, are formed when the transition between one ground state and the other is degenerate, as in poly(acetylene).[28] If that is true, then the two states of poly(DHBZCOT) are nearly degenerate; whereas, the two states of poly(BZCOT) differ by about 30 kcal due to the loss of benzene resonance (Figure 3).

Poly(acetylene)

Poly(BZCOT)



Poly(DHBZCOT)

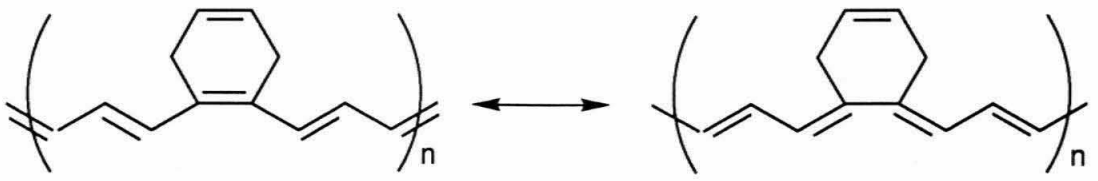


Figure 3: Geomertic isomers of poly(acetylene), poly(BZCOT) and poly (DHBZCOT

Since these states are not degenerate, formation of solitons is not likely to occur, as in the case of poly-pyrrole, but bipolarons could be formed. The band gap for both poly(BZCOT) and poly(DHBZCOT) is about 2.75 eV. It is unclear why there is little difference in the band gaps of the two polymers when one has a degenerate ground state and the other does not. Neither oxidative or reductive electrochemical doping is reversible for poly(BZCOT); yet, reductive doping in poly (DHBZCOT) demonstrates some reversible capability. Chemical doping with iodine shows a 10^3 S/cm difference in conductivity when measured in air. Therefore, a soliton should not be stabilized as well in poly(BZCOT) as it is in poly(DHBZCOT).

Ring-opening metathesis polymerization has again aided in synthesizing random chain bridged polymers which are soluble in

the cis configuration, yet aggregate in solution when photoisomerized to the predominately trans configuration. The enforced cis bond appears to cause an increase in the band gap of the polymer as compared to unsubstituted poly(acetylene).[29] The conductivity of poly(BZCOT) agrees with findings that it is not necessary to have an extensive conjugation length to observe conductivity in a polymer. Chain twist around the polyene backbone was minimized through the use of planar substituents, but the 1,3- and 1,4-hydrogen interactions and the cis bond appear to be enough to disrupt the effective conjugation length of the polymers.

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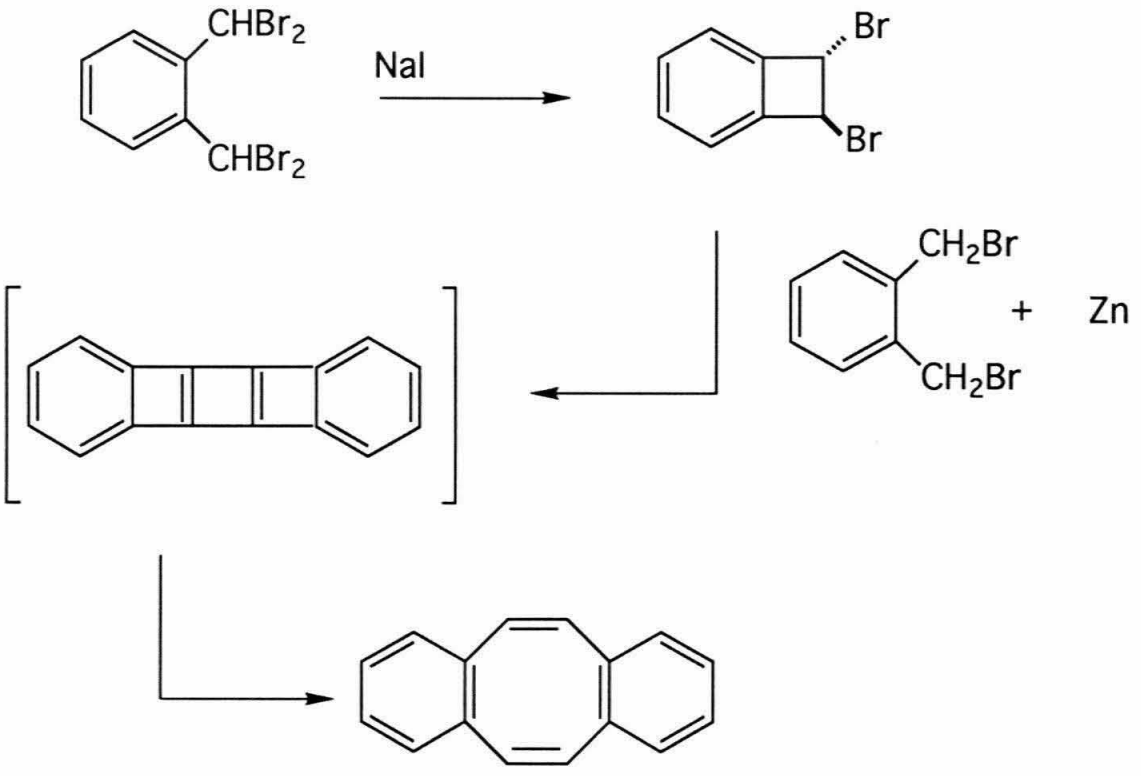
Appendix

Synthetic Routes to poly(ortho-phenylenevinylene), poly(meta-benzo-tetramethylacetylene), and poly(F_pCOT)

I. Monomer synthesis of Dibenzo[a,e]cyclo-octene for Poly(orth-vinylene-phenylene) via ring-opening metathesis polymerization

A. First Reaction Pathway[1]

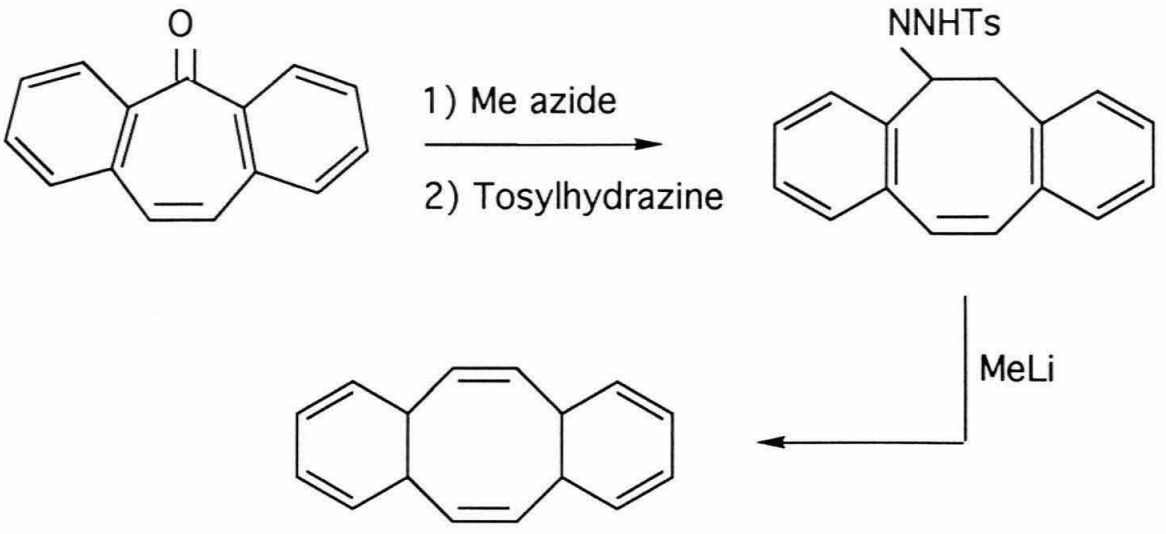
1. Reactions:



2. Only the dibenzo[a,e]cyclo-octane was formed. Synthesis was performed once.

B. Second Reaction Pathway[2]

1. Reactions:



2. Reaction pathway never tried, but seems viable

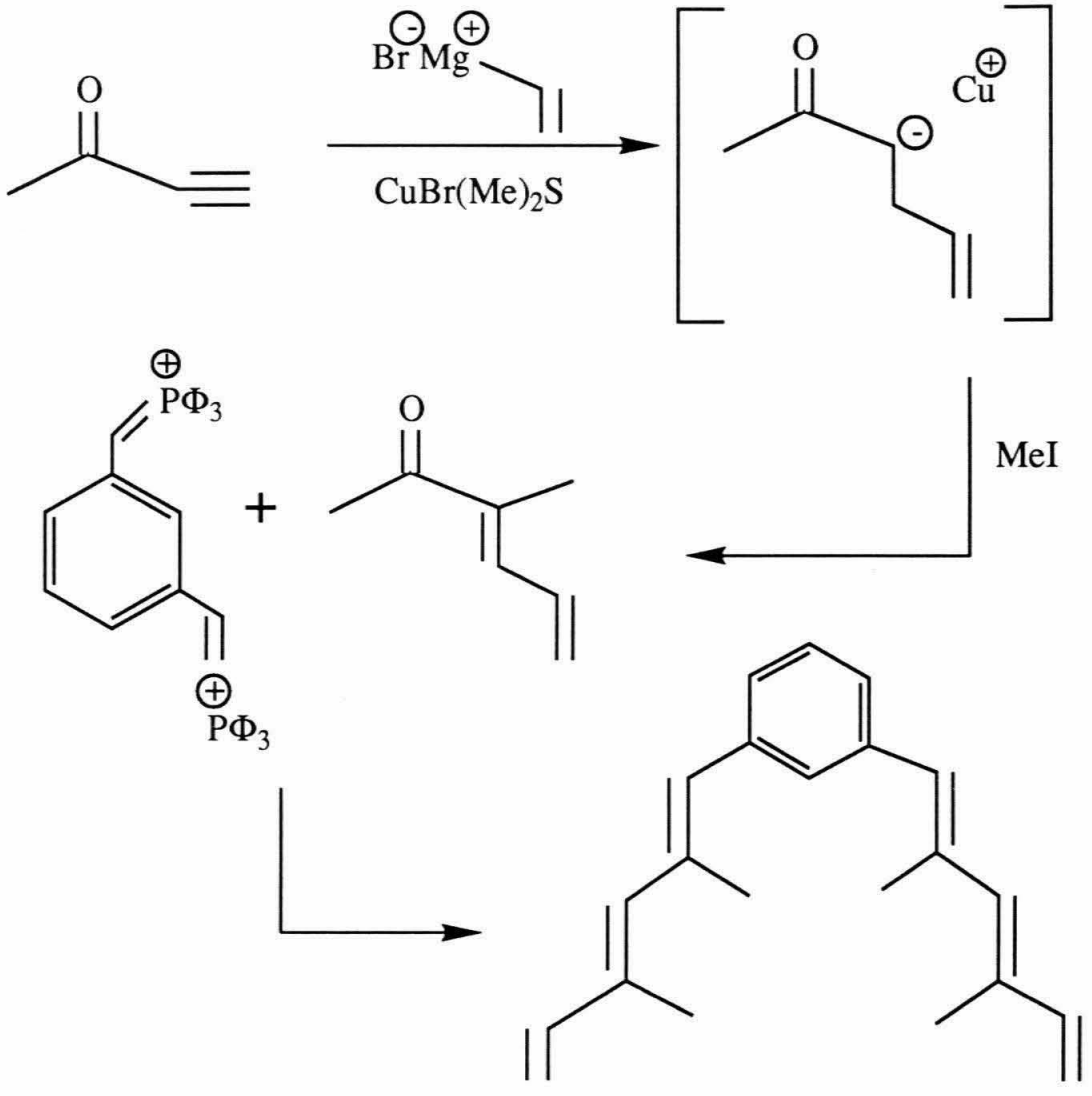
C. ROMP-ing with LKJ's W-catalyst should be effective in creating desired polymer.

II. Poly(para-phenylene-vinylene)

A. [2.2] cyclophane, made by S.C.Virgil, was ROMPed in a 150:1 ratio with LKJ's W catalyst in a 1:1 mixture of pentane and benzene. Yellow polymer crashed out as it was formed. It was not found to be soluble in any other solvent.

III. Meta-(2,3-dimethyl-2,4,6-hexatriene)benzene monomer for acyclic diene metathesis

A. Reaction:



B Experimental:

1. 4-methy-1,3-hexadiene-5-one[3] : Cuprous bromide-dimethyl sulfide (12.5 g, 60.78 mmol) is dissolved in diethyl ether (75mL) and cooled to -45°C. Vinyl magnesium bromide (60mL from a 1M solution in THF, 60.78 mmol) was added, and the solution turned from orange to gray, to black. Reaction mixture left to stir for 2

hours. Warmed to -25°C , added 3-butyne-2-one(3.5 mL, 50.65 mmol), and stirred for 2 more hours. Iodomethane (3.8 mL, 60.78 mmol) was added and, again, reaction was left to stir for 2 hours. Quenched with 25 mL of saturated ammonium chloride, adjusted pH with ammonia and stirred in air for 90 minutes. Separated layers and extracted organic layer once with a solution of saturated ammonium chloride, once with a solution of saturated sodium chloride. Back extracted combined aqueous layers twice with diethyl ether, and dried combined organic layers over magnesium sulfate. Removed solvent in vacuo to yield an orange-brown slurry. Purified by flash chromatography using 10% ethyl acetate/hexane as the eluent; R_f = 0.18. GC/MS shows peak at m/z (%): 55(), 65, 72, 79, 81, 91, 95, 109 M^+(%)

2. 1,3,5-phosphonium-benzene[4]:

a) 1,3,5-benzene-tri-methylester:: 1,3,5 benzene tricarboxylic acid (50 g, 237.94 mmol) was dissolved in methanol (600 mL) and concentrated sulfuric acid (10 mL). Reaction was stirred for 18 hours. A white solid is filtered off, and methanol was concentrated to yield the rest of the product. Total yield 75-81%.

b) 1,3,5-benzene-tri-ol: Lithium Aluminum Hydride (9.26 g, 257.7 mmol) was dissolved in THF (450 mL) and heated to reflux. 1,3,5-benzene-tri-methylester (10 g, 39.6 mmol) was dissolved in THF (150mL) and added via addition funnel to the reaction over a period of one hour. Reaction was stirred 18 hours; reaction had turned from light green to grey. It was quenched with 10 mL water, 10 mL 10% sodium hydroxide and 30 mL water. Filtered off white granular substance and concentrated filtrate to yield a yellow solid.

Crude product was recrystallized in ethyl acetate. Total yield = 44%.

c) 1,3,5-tri-bromo-benzene: A suspension of 1,3,5 benzene tri-ol (1.0 g, 5.946 mmol) in diethyl ether (60 mL) was cooled to 0°C. Phosphorous tribromide (1.77 g, 6.45 mmol) in 10 mL diethyl ether was added dropwise. Reaction was left to stir for 5 hours. Reaction mixture was poured over ice and aqueous layer was extracted with ether (3 times 75 mL). Combined organic layers were dried over magnesium sulfate, and solvent was removed in vacuo to yield a yellow solid. Recrystallized to yield a gray-white solid 82%.

d) 1,3,5-tri-phosphonium-benzene: 1,3,5 tri-bromo-benzene (0.5 g, 1.59) and tri-phenyl phosphine (1.87 g, 7.15 mmol) were dissolved in dry DMF (15mL). Reaction was heated to reflux and left to stir for 16-18 hours. Concentrate reaction mixture and recrystallize.

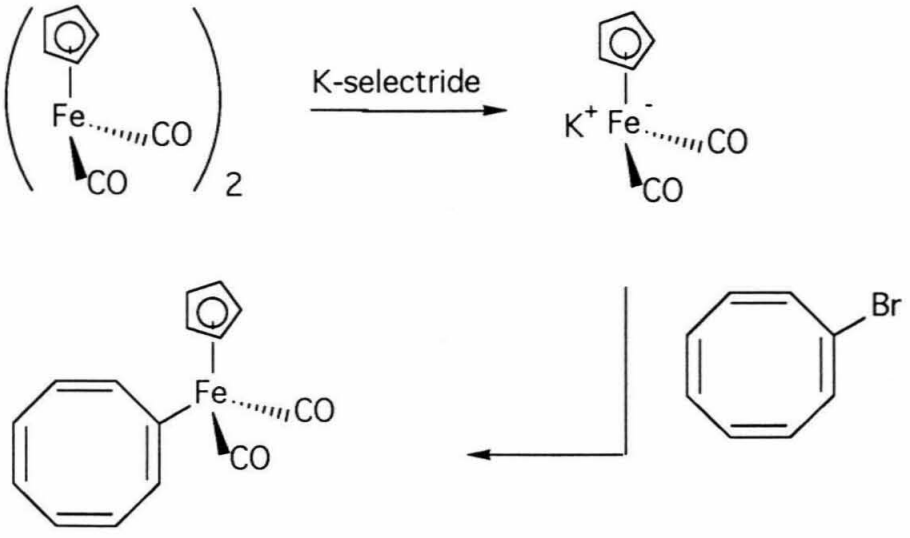
3. 4-methyl-1,3-hexadiene-5-one and 1,3,5-tri-phosphonium-benzene should be coupled via a Wittig coupling to yield desired monomer.

D. The final two intermediates have been synthesized, but not coupled.

E. The 1,3-phosphine salt can also be made.

IV. (Iron cyclopentadienyl dicarbonyl)COT[5]

A. Reaction:



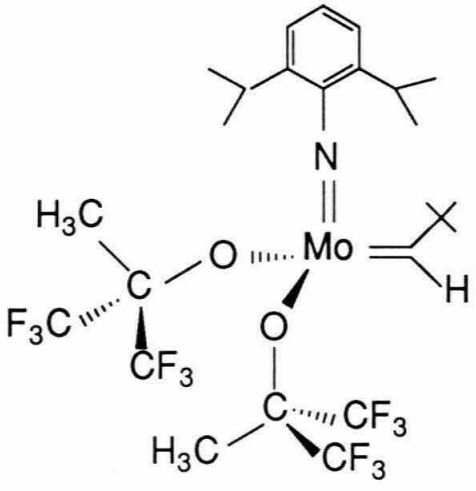
B. Experimental: K-selectride (3.14 g, 14.12 mmol) and Iron cyclopentadienyl dicarbonyl dimer (5.0 g, 14.12 mmol) were suspended in THF (200 mL) and stirred for 3 hours. Cannullated the mixture into a solution of BrCOT (2.6 g, 14.12 mmol) and 200 mL THF and allowed reaction to stir overnight. Concentrated reaction to yield a brown sludge. Attempted to purify via air-sensitive flash chromatography using neutral alumminum oxide and hexane as the eluent. Total yield = 0%.

D. Reaction only tried once; did not master air-sensitive flash chromatography technique.

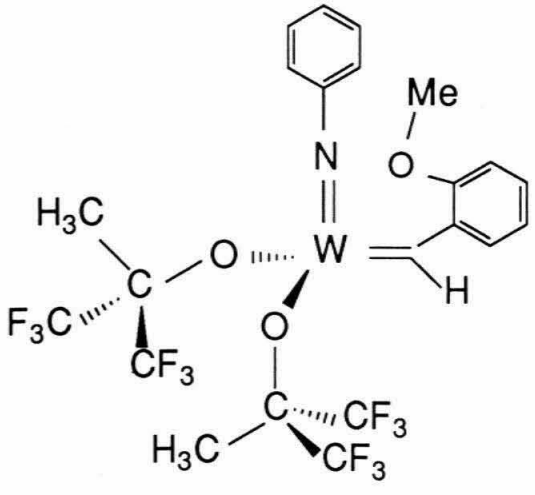
E. Catalyst

1. The following tungsten and molybdenum catalyst were mixed into separate NMR tubes with iron cyclopentadienyl dicarbonyl dimer to determine if the carbene is stable in this environment.

a)



b)



2. The NMR's show that the Mo carbene appears to be stable for at least twenty-four hours.

a) Initial NMR of iron complex and catalyst upon mixing (C_6D_6) in ppm: d = 4.21(5H, C_5H_5) from Cp ring; and d = 12.06 from the catalyst carbine.

b) NMR after 24 hours (C_6D_6): d = 4.21(5H, C_5H_5) from Cp_pring; and d = 12.06 from the catalyst carbine.

3. The W carbine does not appear to be stable.

a) Initial NMR of iron complex and catalyst upon mixing (C_6D_6) in ppm: d = 4.21(5H, C_5H_5) from Cp ring; and d = 10.51 from the catalyst carbine.

b) NMR after 24 hours (C_6D_6) in ppm: d = 4.21(5H, C_5H_5) from Cp ring; and no carbene peak.

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